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A Comparison of Natural and Man-made Hydrocarbon Emission Inventories Necessary for Regional Acid Deposition and Oxidant Modeling

by

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16. ABSTRACT

A biogenic hydrocarbon emission inventory system was developed for the northeastern United States with design options for extension to other areas. Emissions from trees, leaf litter, crops, grass, and water are estimated for cells of 1/6 degrees latitude by 1/4 degrees longitude (about 20 km x 20 km). Hourly emissions were calculated for the period, July 23-26, 1980, and compared with anthropogenic hydrocarbon emissions from the NAPAP inventory. Natural hydrocarbons appear to represent 60% of the regional VOC emissions. Output from the biogenic inventory is structured to provide isoprene and other VOC input compatible with the Carbon Bond IV photochemical kinetic reaction system employed in the Regional Oxidant Model.

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Abstract

The effect of natural hydrocarbon emissions on ozone formation has been a topic of interest for several years and is now receiving additional attention because of the potential influence of ozone in the production of acid species. Because the atmospheric chemistry of sulfur dioxide, nitrogen oxides, and reactive organics is so intricately coupled, natural hydrocarbon emissions have become an important input requirement for both regional acid deposition and oxidant models. A greater emphasis has been placed on treating key chemical components individually in the chemical mechanisms of the models. Applying this concept to emission requirements, there is a greater need for more resolved natural and man-made hydrocarbon emissions estimates.

This paper focuses on natural sources by presenting a method of estimating natural hydrocarbon emissions which is detailed enough to provide quantitive estimates of isoprene and monoterpene emissions from individual vegetation species. This finely gridded natural hydrocarbon emissions inventory was prepared for the northeastern United States and is compared with man-made hydrocarbon emissions over the same area. Natural hydrocarbon emissions represent 60% of the regional hydrocarbon emissions, completely dominating in the non-industrial states. The influence of these natural emissions on the spatial variation of NO_x to HC ratios is presented. The initial concentration ratios of these two species have a significant impact on model predictions of sulfuric and nitric acids, ozone, and hydrogen peroxide. A thorough understanding of the magnitude and distribution of natural hydrocarbon emissions is essential for proper interpretation of regional model predictions.

Introduction

Regional scale models of acid deposition and photochemical oxidants are being developed for two main purposes: 1) a better understanding of the complex interrelationships of emissions, atmospheric transport, and chemical and physical transformations and removal, and 2) use in regulatory analysis to determine source receptor-relationships and effectiveness of proposed control strategies. In either case a complete emissions inventory is necessary for effective use of the models. In the past emissions data used in urban modeling studies were limited to emissions from man-made sources. Recent studies (1) suggest that current estimated emissions rates of biogenic sulfur and nitrogen compounds appear too low relative to anthropogenic emissions to be of major concern. However, the impact of biogenic hydrocarbon emissions on ozone formation especially on a regional scale still remains a topic of debate. Ozone has been shown to have damaging effects on human respiratory tissue and vegetation. And there is growing evidence to support the hypothesis that ozone, and acid precipitation interact to affect natural vegetation and agricultural crops (2).

To enable the regional models to adequately treat ozone formation and the complex chemistry relating oxidants to the formation of acid species in both atmospheric and cloud chemistry, two major components are necessary: 1) chemical kinetics mechanisms which simulate the key chemical reaction pathways and 2) a reliable, complete, and finely resolved emission inventory consistent with regional modeling requirements.

The purpose of this paper is to describe the procedures used to compile a biogenic hydrocarbon emissions inventory in the northeastern U.S. and to characterize the distributional differences between biogenic and anthropogenic emissions. This work was accomplished to provide a gridded, hourly biogenic hydrocarbon inventory compatible with input requirements for the U.S. Environmental Protection Agency's Regional Oxidant Model (ROM). The procedures discussed here can be used to compile a biogenic hydrocarbon inventory compatible with the requirements of the Regional Acid Deposition Model (RADM) currently being developed as part of the National Acid Precipitation Assessment Program (NAPAP).

Biogenic HC Emissions Inventory Development

Three basic components are required to develop estimates of hourly biogenic hydrocarbon emissions with spatial resolution suitable for input into contemporary regional oxidant or acid deposition models: 1) emission factors representative of vegetative species indigenous to the modeling region, 2) empirical relationships between emission factors and specific environmental parameters such as temperature, solar intensity, geographic location, soil conditions, etc. which may influence those factors, and 3) quantitative estimates of vegetation density of the representative species in a designated area. Simply stated, biogenic hydrocarbon emissions for an individual vegetative species are estimated by multiplying an hourly emission factor (μg/g/h) by individual species biomass (dry foliar weight in grams) per grid cell. Total emissions per grid cell are the sum of the individual species emissions. The approach presented here is conceptually the same that has been applied in compilation of previous biogenic

hydrocarbon emissions inventories. The major difference is in the level of resolution of the emission calculation. Emissions estimates are made for individual tree species in contrast to the lumped categories such as deciduous, coniferous, grasses, etc. or isoprene-emitting hardwoods, non-isoprene emitting hardwoods, and conifers used by previous inventory compilers.

Emission Factor Compilation

The scope of this effort was primarily limited to using emission factors obtained from the literature. However, at least one emission factor measurement program in direct support of the Regional Oxidant Model (ROM) development was carried out in Pennsylvania (3) to establish natural hydrocarbon emission rates for the predominant vegetation species in a state considered representative of the ROM domain. As seen in Figure 1 the model domain includes all or part of 15 Northeastern States, the District of Columbia and portions of Quebec and Ontario Provinces in southern Canada. A summary of the emission factors is presented in Table I. Isoprene emission factors have been standardized to 30°C and monoterpene factors have been standarized to 29°C. Emission factors reported in the literature comprise several combinations of hydrocarbon species:

Table I. Biogenic emission factors, biomass and species emissions contribution in ROM domain.

Common Name	Standardized Emission Factors (μg/g/hr) Isoprene	Monoterpene	Biomass (grams X 10**10)	% Total Land Area Covered	% of Total Biogenic TNMHC Emissions
Deciduous Trees	-				
White Oak	10.1	5.6 (D)	580.	2.6	4.7
* Post Oak	12.4 (C)		60.	.24	.35
Chestnut Oak	3.9	1.0 (D)	490.	2.1	1.2
* Chinkapin Oak	12.4 (C)		.88	.00	.01
* Swamp White Oak	12.4 (C)		18.	.09	.12
Northern Red Oak	8.2	3.2 (D)	730.	3.0	3.8
Black Oak	12.4	0.9 (D)	500.	2.2	3.1
Scarlet Oak	14.9	2.8 (D)	7.1	.03	.08
Southern Red Oak	16.0 (C)		69.	.28	.61
* Paper Birch		6.7 (D)	240.	.80	.86
* Yellow Birch		6.7 (D)	270.	.98	.99
Sweet Birch		6.7 (D)	200.	.86	.82
* Gray Birch		6.7 (D)	31.	.04	.12
* River Birch		6.7 (D)	4.4	.02	.02
* Sugar Maple		4.6 (D)	950.	4.1	2.4
Red Maple		4.6 (D)	1600.	6.5	5.7
Silver Maple		3.2 (D)	8.4	.01	.02
* Boxelder Maple		4.6 (D)	59.	.27	.17
* White Ash		0.5 (A)	390.	1.7	.12
* Green Ash		0.5 (A)	140.	.65	.05
* Black Ash		0.5 (A)	8.1	.01	.00
Eastern Cottonwood	32.0		2.1	.01	.02
* Balsam Poplar	43.4		4.3	.04	.02
* Quaking Aspen	43.4		300.	1.3	4.4
* Bigtooth Aspen	43.4		46.	.38	.36
American Elm		3.0 (A)	140.	.64	.30
* Shagbark Hickory		3.0 (D)	40.	.19	.07
Mockernut hickory		3.0 (D)	47.	.21	.14
Pignut Hickory		1.7 (E)	26.	.15	.03
* Bitternut Hickory		3.0 (D)	260.	1.2	.49
Black Walnut		3.0 (D)	40.	.18	.08
* Butternut		3.0 (D)	.26	.00	.00
American Beech		3.8 (D)	470.	1.8	.99
Black Cherry		2.8 (D)	380.	1.6	.61
* Eastern Hophornbeam		11.6 (E)	3.5	.02	.02
American Basswood		3.9 (A)	96.	.45	.20
American Sycamore	17.3 (C)		11.	.05	.09
Black Tupelo Gum		6.6 (E)	68.	.34	.30
Black locust	11.7 (C)		52.	.23	.26
Sweet Gum	11.0	55.5 (E)	54.	.22	2.6
Yellow poplar		5.5 (E)	260.	1.1	.95
Cucumber Tree		5.5 (E)	8.2	.04	.03
Sassafras		7.9 (D)	8.1	.07	.02

Table I (Cont). Biogenic emission factors, biomass and species emissions contribution in ROM domain.

Common Name	Standardized Emission Factors (µg/g/hr) Isoprene	Monoterpene	Biomass (grams X 10**10)	% Total Land Area Covered	% of Total Biogenic TNMHC Emissions
Coniferous Trees					
Eastern White Pine		17.5 (E)	990.	3.3	9.9
* Red Pine		13.2 (E)	130.	.64	.77
Shortleaf Pine		14.7 (E)	92.	.41	.92
Virginia Pine		20.4 (E)	270.	1.4	3.8
Pitch pine		16.7 (E)	140.	.66	1.6
Loblolly Pine		6.0 (E)	140.	.49	.60
Longleaf Pine	1.2 (A)	5.5	.02	.00	.00
* Pond pine		13.2 (E)	.20	.00	.00
Jack Pine		20.4 (E)	43.	.30	.15
* Balsam Fir		13.2 (E)	1100.	2.3	7.8
Eastern Hemlock		2.8 (E)	890.	3.2	1.4
* Black Spruce	10.9	2.2	250.	.85	1.2
* Red Spruce	10.9	2.2	390.	.65	1.8
* White Spruce	10.9	2.2	47.	.06	.21
* Northern White Cedar		2.3 (B)	300.	1.1	.32
Eastern Red Cedar		2.3 (B)	54.	.19	.07
* Atlantic White Cedar		2.3 (B)	30.	.09	.05
* Tamarack		2.3 (B)	19.	.05	.12
Agricultural Crops					
Corn		2.3 (D)	NA	14.	30.
Tobacco		0.6 (D)	NA	.16	.01
Tomato		48.1 (E)	NA	.16	.03
Soybean	0.03		NA	4.4	.03
* Alfalfa	59.7(C)		NA	6.3	.09
* Barley		54.5 (B)	NA	.30	.01
* Oats		54.5 (B)	NA	2.1	.04
* Potato		48.1 (E)	NA	.33	.05
* Rye		54.5 (B)	NA	.00	.00
* Wheat	59.7(C)		NA	1.7	.03
Grasses					
Urban grass		189. (B)	NA	1.6	.13
Field grass		189. (B)	NA	14.	1.1

* Actual emission factor (EF) data not available; an EF for a smiliar species was substituted.

(A): TNMHC without isoprene and monoterpene
(B): TNMHC including monoterpene
(C): TNMHC including isoprene; monoterpene may or may not be present
(D): TNMHC without isoprene; monoterpene may or may not be present
(E): TNMHC including monoterpene but without isoprene.

- isoprene only (I)
- monoterpene only (M)
- total non-methane HC without isoprene and monoterpene (A)
- total non-methane HC including monoterpene (B)
- total non-methane HC including isoprene; monoterpene may or may not be present (C)
- total non-methane HC without isoprene; monoterpene may or may not be present (D)
- total non-methane HC including monoterpene but without isoprene (E)

Some model chemistry mechanisms, for example the Carbon Bond IV mechanism used in ROM (4), treat isoprene explicitly in contrast to monoterpenes which are lumped into carbon bond or reactivity categories. To be consistent with these mechanisms, biogenic emissions must be separated into appropriate categories. Table 2 lists the assumptions that are applied to separate isoprene and monoterpene emissions when total non-methane (TNMHC) hydrocarbon emission factors are used. Subsequently, monoterpenes are split into carbon bond or reactivity categories as required by the specific chemistry mecnanism.

Table 2. Percentage distribution of TNMHC emissions

	Isoprene	Monoterpene	Unidentified
Class A			100
Class B	20	50	30
Class C	50	20	30
Class D		20	80
Class E		50	50

An additional assumption that 25% (by weight) of unidentified hydrocarbons mass is monoterpene was applied to each emission factor class; thus Class A which is entirely unidentified hydrocarbon is assumed to contain 25% monoterpene. Since most of the unidentified hydrocarbons are thought to be fairly nonreactive their inclusion may tend to bias emission estimates upward.

There are several other sources of uncertainty associated with current emission factors found in the literature (3). The measurement techniques used to derive emission factors are estimated to have approximately ±20% error associated with the enclosure measurement technique and ±14% associated with the concentration gradient approach. Also, specific emission factors are not available for all vegetation species in the model domain, thus known factors from similar species were substituted for missing data. Species for which this assumption was made account for 23% of the total hydrocarbon emissions in the domain.

Environmental Effects on Emission Factors

Emission factors are known to vary with many environmental factors such as temperature and light intensity. Geographic location, soil conditions, and elevation are thought to be important also. The effects of light and temperature on live oak isoprene emissions have been investigated by Tingey (5,6). Empirical relationships developed from this research were used to adjust the standardized emission factors for isoprene emitting vegetation to specific hourly light intensity and ambient temperatures in each grid cell. Clear sky conditions were assumed, therefore emission

factors are adjusted to a maximum with regard to light intensity. Light attenuation due to clouds and aerosols may be incorporated in future emissions calculations. Tingey's temperature relationships were developed using leaf surface temperature. Because this measurement is not readily available on a regional scale, ambient temperature is used as a surrogate, thus enhancing the possibility of underestimating the emission factors (7). The underestimation due to the ambient temperature surrogate may balance the overestimation due to the clear sky assumption. These light and temperature dependencies are assumed to apply to all isoprene emitting species based on research results of Sandze and Kalandadze (8,9) which indicates similar relationships for species other than live oak.

Monoterpene emissions do not appear to vary with light intensity (6) thus standardized monoterpene emission factors are adjusted for hourly ambient temperature according to empirical relationships determined by Tingey (10) in his study of slash pine saplings. The influence of other environmental parameters on biogenic hydrocarbon emission factors have not been adequately quantified and thus are not applied in this effort.

Estimation of Gridded Biomass

Biogenic hydrocarbon emissions emanate from living surface vegetation composed of trees, shrubs, grasses, agricultural crops, decaying leaf litter and vegetation in fresh and salt water. Emission factors have been obtained for many individual vegetation species within these general classes and thus it is most appropriate to estimate biomass for each individual species within a class. This provides flexibility to update

individual emission factors and the information necessary to evaluate the importance of individual vegetation species in a specific area.

The raw data used to quantify the predominate vegetation types in the ROM domain were obtained from several sources: U.S. Department of Agriculture Forest Service (USFS) Resource Bulletins (11-27), Oak Ridge National Laboratory's (ORNL) Geoecology Agricultural Data File (28), Rand McNally & Co., Premier World Atlas and Road Atlas (29,30). The USFS tree inventories for each of the 16 States in the ROM domain are compiled from aerial photogrammetry techniques supplemented with spot verification from randomly located plots within stratified forest types. All areas of one acre or greater are included. Each bulletin lists the number of each predominant tree species in 10-12 diameter breast height (dbh) classes, and total area by USFS geographic region for commercial and non-commercial forest, productive-reserve forest, water area, urban area, and agricultural area. Older bulletins do not have the number of trees data for the two dbh classes less than five inches. In most cases the responsible USFS Experimental Station was able to provide these data, otherwise they were estimated from state level totals for hardwoods and softwoods which are in the bulletins. Some of the smaller states such as Rhode Island, Delaware, and Connecticut, are each designated as a USFS region whereas larger states are divided into several regions, typically four to eight. Also the 1978 Census of Agriculture incorporated as part of ORNL's Geoecology Data Base provides land area by individual major crop species within each county. This data base also contains county level information on crop yields, natural vegetation areas, tree species growing-stock volumes, and land use. Fresh and salt water areas within each region were derived from the Rand McNally Atlases.

These raw data in conjunction with the National Land Use and Land Cover Inventory (LUCI) developed by EPA's Environmental Monitoring Systems Laboratory-LV (31) were used to estimate gridded biomass for each vegetation specie. Data for LUCI were derived from the U.S. Geological Survey's Land Use and Land Cover map series (1:250,000 scale), from LANDSAT regional mosaic images, and from single-scene LANDSAT spot coverages. The resolution from LUCI is generally 40 acres and larger.

Land use area coverage in each grid cell (1/4° longitude by 1/6° latitude) is estimated to the nearest 5% for each of the following categories

1) urban
2) agricultural
3) rangeland
4) deciduous forest
5) coniferous forest
6) mixed forest (including forested wetland)
7) nonforested wetland
8) water
9) barren land
10) rocky open area (lichen, low shrubs)
11) mixed agricultural and rangeland

Data have been compiled for the entire continental U. S. and portions of southern Canada. The last three categories did not occur in the ROM domain.

The first step in the gridding procedure is to calculate the distribution of vegetation species within each USFS region. Canopy area for each tree species in a region is calculated using an empirical relationship between diameter breast height (dbh in inches) and canopy area developed by Krajicek et. al. (32).

canopy diameter (feet) = 1.829 x dbh + 3.12, for deciduous species

canopy diameter (feet) = 1.313 x dbh + 5.06, for coniferous species

For each species, the number of trees in a given dbh class is multiplied by the derived canopy area for that dbh class. The resulting values for the 12 dbh classes are summed to yield the effective canopy area for each tree species in the region. The proportional distribution of tree species over the region is calculated by dividing the effective canopy area of a species by the sum of the canopy areas for all species in its major category (deciduous or coniferous). Crop distributions were calculated using county-level yield and crop areas summed to the regional level and divided by the total agricultural area in the region. This proportional distribution of vegetative species is applied to each grid cell in the region in conjunction with gridded land use areas from the LUCI.

Foliage weight for each tree species can be estimated from allometric relations between different dimensions of the tree. For this study, diameter at breast height (dbh) was linearly related to dry foliage biomass in the logarithms of the two dimensions. Beauchamp and Olson (33) discuss the median estimate that logarithmic relations provide and the necessity to correct to the arithmetic mean when calculating cumulative mass. A satisfactory calculation for y, the dry weight foliage, is provided by:

$$y = \exp(A + B\ln(x) + s^2/2), \text{ where}$$

y = the estimate of y in grams for x in cm

B = slope coefficient of ln(y) on ln(x)

A = intercept of $\ln(y)$ on $\ln(x)$

s^2 = sample variance of the logarithmic equation

All the individual raw tree data from Sollins and Anderson (34) with dbh > 2 inches and the corresponding foliage weight, except data set 13, were used to develop separate allometric relations for coniferous and deciduous species. These were:

$$y\ (\text{coniferous}) = 94.875 * (\text{dbh})^{1.514} * 1.070$$

$$y\ (\text{deciduous}) = 20.589 * (\text{dbh})^{1.754} * 1.293$$

where the last terms in the equations are the correction factors. These relations were used to calculate the dry foliage weight for a tree characterized by the midpoint of a diameter class. The sum over diameter classes of the product of the characteristic mass and the number of trees in a class gives the total foliar biomass. This is calculated for each tree specie and the resulting mass distributed within the grid proportional to forest area for softwoods or hardwoods as appropriate. The estimates for conifers in larger diameter classes are less than four percent of the total green weight in the same classes which is an alternate approximation of foliar biomass (35).

Water, leaf litter, and crops use emission factors that are area dependent and therefore do not require gridded biomass. Gridded water areas are directly available from the LUCI data. Leaf litter is calculated as the total forest canopy area minus the area occupied by tree trunks, which is negligible.

Anthropogenic Emission Inventory

The anthropogenic emissions of hydrocarbon and nitrogen oxides presented here were developed by the Emissions and Controls Task Group (TG-II) of the National Acid Precipitation Assessment Program (NAPAP) (36). Basic data for a 1980 base year inventory were extracted from the Environmental Protection Agency's National Emissions Data System (NEDS) and updated by incorporation of improved emission factors and extensive quality control. Annual emissions are provided for both point sources greater than 100 tons/year and area sources at county resolution. Most regional scale Eulerian models such as RADM and ROM required input emissions with finer temporal, spatial, and species resolution. Thus allocation factors were developed to apportion 1980 annual emissions into the hourly gridded (1/4° longitude by 1/6° latitude) emission species required by the specific chemistry mechanism of the regional models. The temporal allocation factors for electric utilities are based on an analysis of hourly power plant fuel use data, whereas operating rate data are used to develop default factors for other industry types in the point source industry. Area source temporal allocation factors vary on an hourly basis for the highway categories and stage II gasoline handling. Allocation factors for residential fuel use categories are season specific for each site with hourly variations dependent on monthly averages of 3 hour meteorological data. Temporal factors for most of the remaining area source categories vary in daily start and stop times and nighttime and weekday operation. Thus the hourly anthropogenic emissions generated by applying these factors represent a "typical" day's emissions rather than reflecting the actual meteorological conditions of a particular day as is the case with the hourly biogenic hydrocarbon emission estimates.

Spatial allocation of county emissions to grid cells is assumed to be proportional to a known distribution of surrogate indicators such as population, housing, land use classification, etc. This is similar to the biogenic emissions methodology which uses gridded land use areas and percentage distribution of vegetative species within a USFS region to spatially allocate emissions.

Anthropogenic hydrocarbon species allocation are based on limited measurement data found primarily in the Volatile Organic Compound (VOC) Species Data Manual and Regional Air Pollution Study (RAPS) reports. These species allocation process is specific to the particular chemistry mechanism in the model.

Results and Discussion

As seen in Figure 1 the ROM domain covers a surface area of approximately one million square kilometers. Using hourly gridded temperature and solar radiation estimates for July 26, 1980 the biogenic TNMHC hydrocarbon in this region are calculated to be 2.6×10^7 kg/day (2.9×10^4 tons/day). Approximately 18% of these emissions are isoprene; 41% are monoterpenes. The remaining 42% are unidentified hydrocarbons which are treated as non-reactive hydrocarbon by the chemistry modules of the regional models and thus have very little effect on the hydrocarbon chemistry. This particular day was chosen because of the high measured ambient ozone concentrations.

The anthropogenic TNMHC emissions for a typical summer weekday for the same region is calculated to be 1.7×10^7 kg/day (1.9×10^4 tons/day). Thus biogenic sources contribute approximately 60% of the TNMHC in the region. If only reactive hydrocarbons are considered the percentage contribution of biogenics to total reactive HC drops to 54%. Figure 2 presents a diurnal profile of total reactive hydrocarbon for four days in July 1980. Since the anthropogenic reactive HC emissions reported here are for a "typical weekday" they do not vary from weekday to weekday, but do drop on July 26, which is a Saturday. Biogenic emissions, in contrast, were calculated using temperature data for July 23 thru July 26, 1980. The average daytime temperature difference between July 23 and July 26 was 2.7°C and resulted in a emissions difference of 4×10^6 kg/day (4.4×10^3 tons/day). Similar temperature effects probably occur with actual anthropogenic hydrocarbon emissions also, but that level of detail is not reflected in the NAPAP emissions inventory. The change in solar zenith angle over the four days is negligible.

It is useful to compare this biogenic hydrocarbon emissions inventory with similar inventories to obtain some level of confidence in at least the order of magnitude of the hydrocarbon estimates. Lamb, Westberg, et al. (3) have estimated biogenic TNMHC emissions for Pennsylvania using daytime and nighttime average emission factors for three categories of trees: isoprene emitting species, non-isoprene emitting species and conifers. These average emission factors were adjusted to 27°C, the climatological average August daytime temperature, and 18°C for the nighttime average. Lamb reported biogenic TNMHC emissions of 2510 tons/day from Pennsylvania forests and 890 tons/day from corn, hay, and pastures.

This compares reasonably well with our estimate of 2920 tons/day from Pennsylvania forests and 1510 tons/day from crops and grasses.

The increase in estimated biogenic hydrocarbon estimates for Pennsylvania is directly attributable to differences in methodology. Lamb uses one allometric equation to estimate forest biomass for all tree types. We use one equation for conifers and a different equation for deciduous trees. Emission factors and associated biomass are calculated for each vegetative species instead of using class averages, and the effect of temperature and sunlight are applied on an hourly basis in contrast to using a monthly average. Thus it appears that a more detailed methodology tends to slightly increase biogenic hydrocarbon emissions estimates. The reliability of emission factors for crops is questionable and the effects of temperature and light are relatively unknown, therefore these emission calculations for crops should be viewed as rough estimates only.

One of the advantages of estimating emissions for individual vegetative species is the ability to evaluate which species are predominant in the region of interest in terms of spatial coverage and emission contributions. Corn covers 14% of the ROM domain and accounts for ~30% of the monoterpene emissions. An additional 5200 tons of unidentified TNMHC emissions from corn are considered unreactive. Given the stated unreliability of crop emission factors and the magnitude of estimated emissions from corn, this vegetation species should receive more attention in future emission factor measurement programs.

Other major contributors to monoterpene emissions are White Pines, Balsam Fir and Red Maple contributing 15%, 12% and 6% to monoterpene emissions respectively. The major isoprene emitting species are Quaking Aspen, Black Oak, and White Oak contributing 25%, 16% and 15% of isoprene emissions respectively. Note on Table I the species marked with an "*" to indicate the lack of a specific measured emission factor. Of these the Balsam Fir, Quaking Aspen and Sugar Maple warrent the most attention.

Biogenic hydrocarbon compounds such as isoprene and monoterpenes have been shown to be very efficient at producing ozone when photoxidized in the presence of NO_x (38). This realization has led to the development of kinetic mechanisms which explicitly include these biogenic compounds (39,40,41). Killus (39) has found that even at low ambient concentrations isoprene can contribute significantly to the reactivity of the rural air through its own reactivity and the production of highly reactive oxidation products. A simplified form of this isoprene mechanism has been incorporated into the ROM. Lack of kinetic and mechanistic data for monoterpenes has hindered development of a reliable explicit mechanism for α-pinene or other monoterpene compounds (40). Given that monoterpene emissions have been estimated to be 41% of the biogenic TNMHC emissions in the ROM domain continued effort on a reliable monoterpene mechanism appears to be warranted.

Arnts and Gay (38) showed that there is an optimum HC/NO_x ratio for maximum ozone formation which is typically lower than what is observed in ambient rural air. This range falls between 1 and 20. HC/NO_x ratios in

the ROM domain are significantly changed in the rural areas by the addition of biogenic hydrocarbon. Ratios based strictly on anthropogenic emissions varied between .03 and 60 with 75% of the values less than 5. When isoprene and monoterpene were incorporated in the calculation of the HC/NO_x ratio the range varied from .01 to 5433 with 75 percentile at 243; the 25th percentile was 41. Thus it appears that the additional biogenic hydrocarbon emissions tend to reduce the ozone forming potential even in the cities where the NO_x concentrations are high.

There are many issues yet to be resolved in terms of the actual contribution of biogenic hydrocarbon to ozone formation. Regional modeling studies incorporating isoprene explicitly and using the more resolved estimates of biogenic emissions should provide useful information to help resolve this longstanding controversy.

Conclusions and Recommendations

A more highly resolved spatial and temporal biogenic hydrocarbon emissions inventory was developed for use with the ROM. There was a 36% increase in ROM peak hourly emissions of reactive hydrocarbons from the first to the fourth day of the modeled period. This was accompanied by an increase of 120% in the peak median hourly ozone observed in the ROM domain between the two days. The change in weather conditions during the four days is independently conducive to an increase in both. A portion of the larger relative increase in ozone may be in part due to the increase of reactive hydrocarbon emissions.

This detailed inventory agrees well with a similar inventory done for Pennsylvania. Biogenic TNMHC emissions were estimated to be larger than the corresponding anthropogenic emissions and thereby contribute 60% of the total hydrocarbon emissions in the northeastern United States. A large portion, 42%, of the hydrocarbon emissions were nonreactive. There was about as much monoterpenes, 40%, and just 18% was isoprene.

Since many species have emission factors assigned based on similarity, measurements should be done on corn, Balsam Fir, Quaking Aspen, and Sugar Maple because of their relatively high contribution. The presumption of nonreactivity for some of the biogenic emissions should also be studied.

A program to provide a monoterpene reaction mechanism for eventual incorporation in the oxidant chemistry modules for both the ROM and RADM is warranted. Regional modeling studies should include biogenic species which are treated explicitly and for which detailed inventories are developed.

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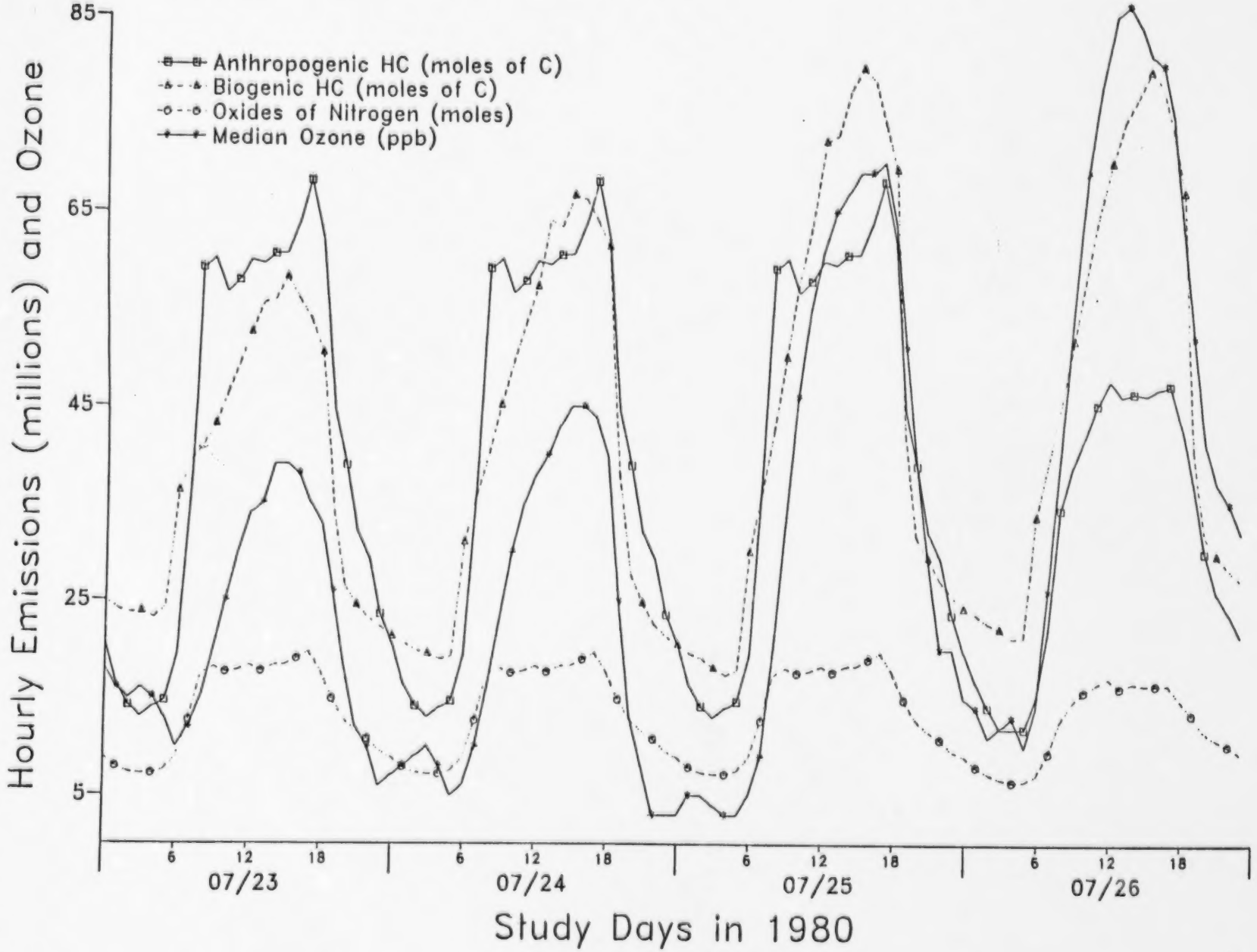

Figure 2. Comparison of anthropogenic and biogenic emissions

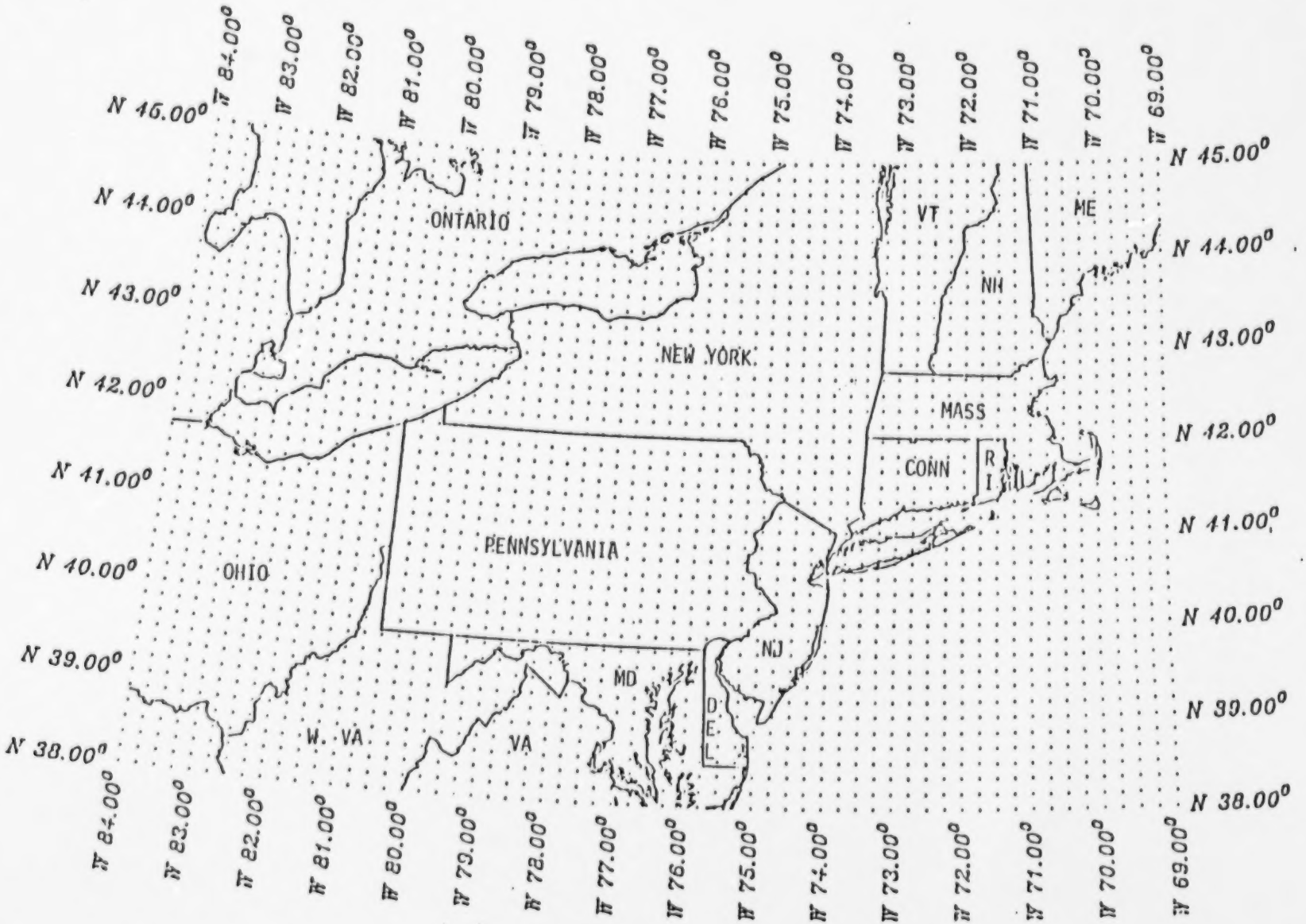

Figure 1. Regional Oxidant Model domain